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Plasma deposition of conductive polymer composites for strain sensor applications

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Abstract

The aim of this work is to develop a large area thin film of a conductive polymer composite (CPC) for large area strain sensor applications. Therefore an alternative plasma deposition process is applied for the manufacturing of CPC as flexible thin films. Plasma polymer films are used as matrix that are deposited with a 60MHz plasma reactor and characterized with dynamic mechanical analyzes (DMA). Copper nanoparticles with different sizes are generated in a special hollow cathode. To enhance the sensitivity of the strain sensor a particle concentration in the matrix at the percolation threshold is important. For this reason, in situ U/I-measurements during particle deposition were done. The characteristics of resistance of the CPC films are analyzed during elongation.

Keywords: PECVD, Plasmapolymer, gas flow sputtering, conductive polymer composites, strain sensor

1. Introduction

Nanoscaled particles embedded in matrix materials have become an interesting ever-growing research field in the last years. It is commonly understood that these “nanocomposite” materials open up completely new fields of research and applications in e. g. materials science[1], sensors[2], optical systems[3], catalysts[4] and renewable energies[5]. For high purity requirements, vacuum processes are an excellent choice: They exhibit low contamination levels, can control thin films on the nanometer thickness scale, and are compatible with the majority of process steps in the high-tech industry (e. g. in electronics, optics). Taking this into account a pilot system for vacuum/gas phase deposition for homogeneous thin films of conductive polymeric nanocomposites (CPC) materials on large areas was built. The concentration of conductive particles in the insolating matrix must be at the percolations threshold to get the highest sensitivity for expansion or shrinking. This composite materials change their conductivity with the influence of external parameters like pressure, strain or organic vapors. Isoprene[9], polyvinylalcohol[6] and different copolymers[7,8] were used as highly flexible matrices. The mechanical properties strongly depend on the crosslinking density of the polymers. Crosslinking during deposition as one-step-process is possible during plasma polymerization by plasma enhanced chemical vapour deposition (PECVD). The properties of Plasma polymers can be tuned by changing of pressure, precursor flow, power-input and duty cycle time. To increase the conductivity of the matrix conductive polymers can be used. For this reason the mechanical properties of poly pyrrole are analyzed. On the other hand, the gas flow sputter source can give copper nanoparticles at controllable sizes[9]. This special type of a hollow cathode allows thermalization and coagulation of the sputtered atoms because of high pressure in the

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plasma region. Clusters are formed in the saturated vapor and sprayed onto the substrate with a continuous gas flow through the hollow cathode[10]. We want to establish plasma polymers as functional matrices for pressure and strain sensitive composites with copper nanoparticles.

2. Experimental

The nanocomposites obtained by alternating deposition of nanoparticles and plasma polymers in a vacuum deposition system is described elsewhere[11]. By changing source parameters (e.g. pressure, power density of the targets) films of practically any useful thickness and particle concentration in the matrix can be obtained. First the matrix and the particles are deposited and characterized separately. Additional first combinations of particles and plasma polymer matrices are investigated. Different plasma polymer layers were deposited to characterize there mechanical properties while deposition parameters kept constant (table 1). The working gas is argon (Air liquide, Paris, France) with purification grade of 5.0. Vinylalcohole, 2-Methyl-1,3-butadiene, and Hexamethylene-disiloxane were purchased from Sigma-Aldrich (St. Louis, USA) and utilized without further purification. Pyrrole (Sigma-Aldrich, St. Louis, USA) is distilled over zinc powder (Sigma-Aldrich, St. Louis, USA) before using.

Table 1: Deposition parameters

power [W]	pressure [Pa]	Ar-flow [sccm]	precursor-flow [sccm]	deposition time [s]
50	43	10	10	1800

Mechanical behavior of the plasma polymer films is investigated with a dynamic mechanical analyzer (DMA 2980, TA Instruments inc. New Castle, USA).

For the experiments the gas flow sputter source was equipped with two copper targets (100 x 50 x 6 mm^3). Copper nanoparticles generated in the system were characterized with SEM and TEM. For a characterization by SEM (Carl Zeiss Gemini 982 DSM, Carl Zeiss Jena, Jena, Germany), the particles were deposited on highly doped silicon wafers in order to have a well conductive substrate. For a better resolution, additional samples were analyzed by TEM (FEI Tecnai T20, Tecnai inc., Hillsboro, USA), for which particles have been deposited on carbon grids (Nano And More GmbH, Wetzlar, Germany).

Finally, composite materials were examined to characterize their electrical bulk properties under stretching as well as microscopic aspects (percolation threshold). Here, for in-situ conductivity measurements during deposition and of nanoparticles during stress applications to the composite films an electrometer (Keithley 237, Keithley Instruments, Cleveland, USA) is used. First tests of the conductive behavior under stress applications are done with composite films on flexible polyimide (kapton®, Du Pont, Wilmington, USA) substrates with gold electrodes.

3. Results and discussion

In a dc gas flow sputter source a flow of inert gas carries atoms sputtered from the targets out of the discharge zone. The sputtered atoms thermalize in the gas phase and condensate to form clusters and nanoparticles [11]. Figure 1 shows TEM images of copper nanoparticles obtained with different power conducted to the targets. The deposition time was kept constant at 45s. At high power densities in the plasma (5000W, 800V, dc) spherical copper clusters at cluster diameters of 2 – 4 nm can be observed. These clusters are single crystalline. At low power densities in the plasma (500W, 400V, dc) agglomeration of clusters to larger particles (30nm), which will hence not show single crystallinity, were observed (figure 5B). The particles are well separated in both images and have the same compact spherical shape. A second effect on particle growth is observed by changing process pressure. The rise of the pressure in the growing zone is going along with an increasing of flow, because the pumping speed is not controlled. As may be seen in

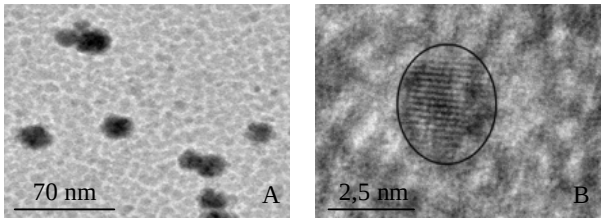

Fig. 1 TEM Images of Cu particles deposited at different power input A: 0,5 KW; B: 5 KW; Pressure 40 Pa, 2000 sccm argon-gas flow

table 2 an increase of process pressure from 56Pa (Ar-flow 2000sccm) to 96Pa (Ar-flow 4000sccm) at 1000W will result in agglomeration of larger particles, too.

Table 2: Sizes of copper particles under different plasma conditions in the gas-flow-sputter source

power [W]	argon flow [sccm]	pressure [Pa]	particle size [nm]
1000	5000	96	24
1000	4000	76	8
1000	3000	56	6
500	1000	36	35
5000	1000	36	3

The deposition rate reaches a maximum at 100nm/min at an Argon flow of 5000sccm.

The storage modulus E’ is important for the dynamic mechanical behaviour of the sensitive layer. It is the part of the applied energy (complex young modulus E*) which is saved for response after deformation. The lost energy in consequence of heat dissipation is described by the loss modulus E’’.
Dynamic mechanical analyzer uses a force of 0,1N with a frequency of 5Hz that is applied to plasma polymer films on polyimid substrates.

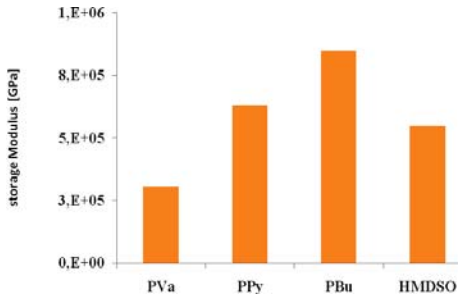

Figure 2: Storage modulus of 1,6µm films of plasma polymers on poly imide substrates (PVa – poly vinylalcohol; PPy – poly pyrrole; PBu – poly butadiene; HMDSO – hexamethylene siloxane)

The storage modulus is the part of the applied force, which is changed into elongation and response after penetration. High values like in the case of poly butadiene are interesting for the possible application as mechanical sensor (Figure 2). But coevally a higher force is necessary for elongation or deformation.

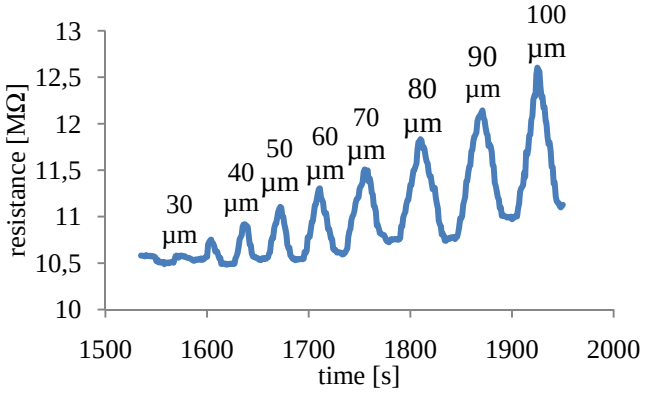

Figure 3: Resistance under different elongations of a copper/polyisoprene-composite film on polyimide

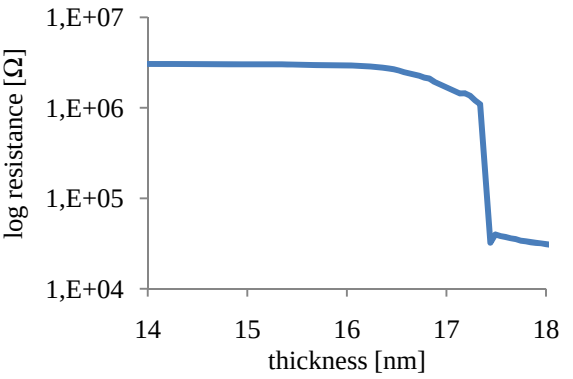

Figure 4: Resistance measured during deposition of copper nanoparticles

Copper nanoparticles are sputtered until the percolation threshold is reached (figure 3) into the polymer matrix to increase the sensitivity for stress-strain applications. Mechanical measurements show a change of resistance of 20% with an elongation up to 3,33% of copper/polyisoprene composites. The resistance is rising after a couple of measurements caused by oxidation of the particles (figure 3).
The resistance of copper/polypyrrole composites increase about 45% with an elongation of 0,007% (tensile strain 25GPa).

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